FWP Summaries

Argonne National Laboratory
Materials Science Division

November 2006

B&R Code	FWP	Title
KC020101	58405	Electron Microscopy Center for Materials Research (moved to facilities)
KC020103	58307	Interfacial Materials
KC020103	58930	*In Situ* Alloy Oxidation
KC020105	58502	Digital Synthesis
KC020201	58701	Neutron and X-ray Scattering
KC020201	58926	Synchrotron Radiation Studies
KC020202	58806	Dynamics of Granular Materials
KC020202	58906	Superconductivity and Magnetism
KC020202	58916	Emerging Materials
KC020202	58918	Magnetic Films
KC020202	58920	Digital Synthesis (text combined with FWP 58502)
KC020203	59001	Condensed Matter Theory
KC020203	59002	Materials Theory Institute
KC020203	59003	Quantum Computation with Electron Spins
KC020301	57504	Nanostructured Thin Films
KC020301	57525	Nanostructured Biocomposite Materials for Energy Transduction
KC020301	58510	Molecular Materials
KC020301	58600	Directed Energy Interactions with Surfaces
KC020301	58601	Fundamental Studies of Electrocatalysis for Low Temperature Fuel Cell Cathodes
KC020301	58806-CD	Collective Dynamics

Laboratory Name: Argonne National Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP:
Interfacial Materials

FWP Number: 58307 (including FWP 58305 through Sept. 2005)

Program Scope: This program combines advanced materials synthesis, complementary *in situ* and *ex situ* characterization and property measurement techniques with computer simulations to elucidate the interfacial contributions to novel phenomena exhibited by thin film oxide heterostructures. The program is structured around three themes: interface control through understanding growth dynamics in complex oxide films, the contribution of interfaces when oxide films are incorporated in heterostructures and developing an understanding of domain behavior in ferroic nanostructures as a function of microstructure and composition. The complementary strengths of simulation and experiment provide fundamental insights into the mechanisms and interfacial driving forces that control composition and microstructure and thus overall film properties.

Major Program Achievements (over duration of support):
In situ studies of ferroelectric thin films: Using a unique integrated MOCVD film growth, x-ray scattering and fluorescence facility at the Advanced Photon Source, we have determined ferroelectric domain wall structure and energetics for the first time in thin films. We have demonstrated the existence of ferroelectricity in epitaxial three unit cell thick $PbTiO_3$ (PTO) films, revealing the thinnest perovskite ferroelectric film that exhibits spontaneous polarization. We have also made a detailed study of the way in which interface and surface environment control domain behavior in PTO, showing that the depolarizing field can be compensated by growth on a conducting underlayer, or by changing the gas environment above the film surface.
Atomistic simulation of ferroelectric perovskites: The first interatomic potentials capturing ferroelectricity in perovskites, including the full phase diagram, were developed and used to study solid solutions and heterostructures.
Studies of complex oxide phenomena at the nanoscale*: In situ* nanoscale studies of growth and interface processes have provided fundamental insight into the barrier properties of novel high-K dielectric alloy oxide layers. We have shown that post-oxidation of a TiAl alloy deposited on Si can be used to produce an amorphous bilayer oxide through segregation of the Ti and Al during oxidation by atomic oxygen. This enables observation of novel transport properties in these materials. We also developed top-down (e-beam lithography) and bottom-up approaches to produce ferroelectric nanostructures and used *in situ* and *ex situ* characterization techniques to reveal previously unobserved 90˚ domain switching dynamics in nanostructures due to released substrate constraints.
Oxide heterostructures: Functionalizing the surface of polarizable ferroelectric lead zirconium titanate films was shown to lead to the possibility of using surface charge to manipulate charged biomolecules such as peptides, opening a new path for research on bio-inorganic oxide interfaces; integrating layers of piezoelectric lead zirconium titanate and ultrananocrystalline diamond enabled the development of piezoactuated diamond-based microelectromechanical/nanoelectromechanical system structures that are enabling fundamental studies of the mechanical properties of these novel heterostructures.

Program Impact: By combining advanced experimental tools and simulation, we have developed an unprecedented understanding of the impact of specific defects (grain boundaries, nonstoichiometry, interfaces) on material behavior. We have established metal-organic chemical vapor deposition as a premier method for the fabrication of high-quality complex oxide films that are recognized as standards against which other films are judged.

Interactions: Internal: Synchrotron Radiation Science (ANL58926), Electron Microscopy Center (ANL58405), Alloy Oxidation (ANL58930), Molecular Control of Synthesis (ANL57504), Advanced Photon Source; External: 16 universities in the US, universities in Argentina, Germany, UK; LBL, industry including INTEL and Seagate.

Recognitions, Honors and Awards (fully or partially supported by this FWP or subtask): Auciello: 2003 Hispanic Engineering Award, 2003 R&D 100 Award, 2006 Federal Lab Consortium Award; Petford-Long: 2005 Election to Fellowship of the Royal Academy of Engineering, 2006 Emile Chamot medal (Illinois State Microscopical Society). Streiffer: 2006 IEEE Ultrasonics, Ferroelectrics, and Frequency Control Society Ferroelectrics Young Investigator Award.

Personnel Commitments for FY2006 to Nearest +/-10%:
A Petford-Long (Group Leader: 100%) O Auciello (100%), G Bai (100%), P Baldo (50%), J Eastman (30%), S Nakhmanson (100% from Sept 06), S Streiffer (50% to Sept 06), L Thompson (80%), D Wolf (70% to Mar 06), J Li (postdoc, 100% to Jun 06), M Tanase (postdoc, 50%).

Authorized Budget (BA) for FY04, FY05, FY06:

FWP58307:	**FY04 BA $**1,695K	**FY05 BA** $1,925K	**FY06 BA** $1,737
FWP58305:	**FY04 BA** $195K	**FY05** joined to FWP 58307	

Laboratory Name: Argonne National Laboratory
B&R Code: KC020103

FWP and possible subtask under FWP:
In Situ Oxide Growth

FWP Number: 58930

Program Scope: This program focuses on providing a mechanistic understanding of the atomic-level and mesoscopic processes associated with oxide nano-island and continuous film growth behavior. Past work has focused on early-stage alloy oxidation behavior, where emphasis was placed on understanding the initial steps of adsorption of oxygen on a clean surface and nucleation of oxide nano-islands, and on later-stage growth, strain development, and creep behavior of continuous, macroscopically-thick oxide layers. Current emphasis is focused on functional oxide thin film growth behavior, including atomic layer deposition (ALD) and oxide MBE of materials including ZnO and complex oxide composites. Our approach uses a unique combination of in-situ synchrotron x-ray and electron microscopy techniques providing structural, chemical, kinetic, and thermodynamic information in controlled environments.

Major Program Achievements (over duration of support):
Alloy-oxide phase equilibria*:* Using in-situ x-ray scattering techniques that we developed at the Advanced Photon Source (APS), we discovered that the pO_2 for equilibrium between Cu_2O nano-islands and Cu differs dramatically from predictions of bulk thermodynamics. This observation has a number of important implications, *e.g.*, for controlling the behavior of supported oxide nano-islands as heterogeneous catalysts of redox reactions.
Compositional effects on alloy oxidation: Insight into alloy segregation behavior in response to oxidizing and reducing gas environments has been obtained through in-situ x-ray and TEM studies. We discovered that alloying Cu with Au leads to substantially slower oxidation kinetics and the formation of oxide islands with dendritic morphology. Studies of Cu-Ni and Pd-Fe alloys have determined the interplay between reversible surface segregation of the more reactive component and the onset of oxide formation.
Strain development and deformation behavior during continued oxidation: We modified the Debye-Scherrer technique to measure growth strains in-situ at the APS with unprecedented accuracy and precision (precision of 10^{-5} in strain). Such in-situ measurements are critical to providing insight into the key processes controlling formation and lifetime of protective oxides.
Reactive element effect: In-situ x-ray experiments determined that the presence of a dilute quantity of Zr or Hf added to β-NiAl changes the stress state of the oxide that forms on the alloy at high temperature from compressive to tensile, leading to dramatic improvement in the performance of the protective oxide.
Strain generation mechanisms in thermally grown protective aluminas: Large strains caused by phase transitions, composition change, internal growth, thermal expansion mismatch (and strain relaxation with creep processes) have been identified and quantified through this program's pioneering in-situ x-ray studies. The unique ability that in-situ techniques provide in separating different strain contributions is essential for understanding oxide development and failure mechanisms.

Program Impact: The program provides fundamental insight into growth behavior of oxide films and nanostructures relevant to a wide range of energy applications, including behavior of materials in extreme environments, solid state lighting, high temperature protective oxide coatings, and energy storage.

Interactions: Internal: Interfacial Materials (ANL58307), Synchrotron Radiation Science (ANL58926), Electron Microscopy Center (ANL58405), Molecular Materials (ANL58510), Advanced Photon Source; External: Lawrence Berkeley National Laboratory, Oak Ridge National Laboratory, Case-Western Reserve University, University of Pittsburgh, University of Illinois-Urbana Champaign, University of Florida, MPI Stuttgart (Germany).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): B. W. Veal and A. P. Paulikas: Listed in Science Watch (vol. 8, p. 1, 1997) among 30 most cited scientists in the physical sciences (1990-1996). B. W. Veal: ANL Exceptional Performance Program, 1992 and 1996.

Personnel Commitments for FY2006 to Nearest +/- 10%: P. Baldo (50%), R.C. Birtcher (70% to May 2006), J.A. Eastman (Group Leader, 70%), H. Iddir (Postdoc, 100% since Aug 2006), A.P. Paulikas (100%), L.E. Rehn (60% to Apr 2006), L.J. Thompson (20%), B.W. Veal (90%), D. Wolf (30% to Mar 2006), G.-W. Zhou (Postdoc, 100%).

Authorized Budget (BA) for FY04, FY05, FY06:
FWP58930 **FY04 BA** $1,396k **FY05 BA** $1,340k **FY06 BA** $1,313k

Laboratory Name: Argonne National Laboratory
B&R Code: KC020105 and KC020202

FWP and possible subtask under FWP:
Digital Synthesis: A Novel Pathway to New Collective States in the Complex Oxides

FWP Number: 58502 and 58920

Program Scope: In our program, we shall create, characterize, control and understand novel states of condensed matter at interfaces of complex oxides using digital synthesis and field-effect doping. These strategies enable the realization and control of a new generation of interfacial systems whose singular characteristic is that they have no explicit disorder. Digital synthesis is a technique where ordered undoped layers are stacked in integer sequences, and all charge transfer or doping takes place at the interfaces. Field-effect doping allows for the introduction of charge at an interface capacitively via gate-electric fields, without the introduction of any additional disorder that are associated with chemical doping.

Major Program Achievements (over duration of support):
Using ozone-assisted oxide MBE, synthesized digital superlattices of $(LaMnO_3)_{2n}/(SrMnO_3)_n$ n=1-5, equivalent to $La_{2/3}Sr_{1/3}MnO_3$ where the *A*-site disorder has been eliminated. Superlattices equivalent to $La_{1/3}Sr_{2/3}MnO_3$ have also been synthesized.
Observed a metal insulator transition driven by proximity between $LaMnO_3/SrMnO_3$ interfaces in the $(LaMnO_3)_{2n}/(SrMnO_3)_n$ superlattices.
Carried out local spectroscopy using STEM-EELS (in collaboration with Robert Klie, STEM group at Brookhaven) to measure the diffusion of holes at a $LaMnO_3/SrMnO_3$ interface in real space, and show how this is affected by the onset of ferromagnetism.

Program Impact:
Novel synthesis forms the heart of this program. We have designed a state-of-the art oxide Molecular Beam Epitaxy system that will be operated as a collaborative user facility at the Center for Nanoscale Materials at Argonne, and will be accessible through on the basis of competitive user proposals.

Interactions:
CNM, MTI and APS at Argonne, LANSCE at Los Alamos, Dr. Yimei-Zhu's group at Brookhaven, University of Illinois at Chicago, Prof. Allen Goldman at University of Minnesota, Dr. Stuart Parkin at IBM, Prof. R. Ramesh at Berkeley.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
5 Invited Talks in 2006 at Brookhaven National Lab, Northwestern University, IBM San Jose, the International Workshop on Mesoscale Superconductivity and Magnetism in Chicago and the MTI/CNM International Fall Workshop on Nanoscale Physics VI at Argonne.

Personnel Commitments for FY2006 to Nearest +/- 10%: Anand Bhattacharya (P.I.) 100%; Samuel D. Bader (10%)**.** We plan to make two Post-Doctoral hires in early 2007. External Subcontracts: Prof. James N. Eckstein, UIUC for $96,156.0; Laura Lewis, BNL for $115,367.0

Authorized Budget (BA) for FY04, FY05, FY06: New program, begun in late FY06.

FWP 58502 and 58920: **FY04 BA** $0 **FY05 BA** $0 **FY06 BA** $720K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020201

FWP and possible subtask under FWP:
Neutron and X-ray Scattering

FWP Number: 58701

Program Scope: Members of the Neutron and X-ray Scattering Group enable the Materials Science Division to pursue strong multidisciplinary research programs that combine state-of-the-art scattering capabilities with materials synthesis, theory, and other experimental tools. Worldwide neutron and x-ray scattering facilities are used but priority is given to research topics that anticipate the full capability of the Spallation Neutron Source. An important goal of the group is to strengthen the neutron user community in the US in preparation for the SNS, and we sponsor an annual summer school on neutron and x-ray scattering as a key part of our strategy. Group members also participate in the conception, design, and review of instrumentation for the SNS. More details are available at http://www.msd.anl.gov/groups/nxrs/.

Major Program Achievements (over duration of support):
Superconductors: A world class research program on the relationship of chemical composition and crystal structure to the properties of superconducting materials has been conducted for many years, recently focusing on the phase diagram of the cobaltates, $Na_xCoO_2 \bullet 4xH_2O$. A new program will focus on the high-pressure synthesis of new layered superconducting materials and their characterization by neutron powder diffraction.
Orbital Correlations, Frustration, and Self-Organization: A comprehensive research program in layered manganites has provided the most detailed models of Jahn-Teller polaron correlations competing with ferromagnetic order in any CMR compound. We have also obtained new insights into spin-state transitions and the competition between long and short-range order in perovskite cobaltites as well as into orbital dimerization in layered ruthenates.
Magnetic Behavior in Constrained Geometries: Argonne scientists pioneered neutron reflectometry applying it to critical problems in polymer science and the magnetism of thin films and multilayers. Applications include studies of long-standing problems such as exchange coupled superlattices and exchange bias in thin films. Recent projects have focused on understanding magnetic interactions at the interfaces between epitaxially grown complex oxide materials with different electronic and magnetic properties, such as ferromagnetic/superconducting superlattices.
Biological membranes: A new effort is being pursued to understand the structure/function relations of biological membranes using model biomembrane mimics which host biologically relevant membrane components. This program will make effective use of new spin-echo techniques being developed by the group as well as existing facilities at the Advanced Photon Source.
SNS Instrument Concepts: Group members are developing two novel neutron scattering techniques, which are the basis for proposals to build dedicated SNS instruments. The first is Spin-Echo-Resolved Grazing Incidence Scattering, which is a new method for the study of biological and polymeric membranes. The second employs a correlation chopper to measure with high efficiency single-crystal diffuse scattering with elastic discrimination. A prototype instrument is being tested at the IPNS. Both methods promise to open up new directions in neutron scattering science.

Program Impact:
Work of the group in many different science areas is recognized worldwide as leading the field and opening new research directions in neutron and x-ray scattering. Close interaction with materials synthesis, other experimental techniques, and theory is a particular strength of the group. The impact of research done by the group is demonstrated by 70 publications with 457 citations, and 64 invited talks at major meetings during 2003-2006.

Interactions:
Group members collaborate with other groups in the Division and with a large number of scientists at universities and other national laboratories, as shown by over 250 coauthors on papers published 2003-2006.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
J. D. Jorgensen: B. E. Warren Diffraction Physics Award (1991), C. E. Barrett Award in Powder Diffraction (1997), Among 100 most highly cited physicists (ISIhighlycited.com); G. P. Felcher: Humboldt Award, 1999; R. Osborn & S. Rosenkranz: University of Chicago Distinguished Performance Award (2006); J. D. Jorgensen, G. P. Felcher & R. Osborn: Fellows of the American Physical Society

Personnel Commitments for FY2006 to Nearest +/-10%:
J. D. Jorgensen (Group Leader) (100%), G. P. Felcher (100%), R. Osborn (100%), U. Perez-Salas (100%), S. Rosenkranz (100%), S. G. E. te Velthuis (100%).

Authorized Budget (BA) for FY04, FY05, FY06:
FWP 58701: **FY04:** **BA** $2169K **FY05:** **BA** $2613K **FY06:** **BA** $2477K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020201

FWP and possible subtask under FWP:
Synchrotron Radiation Studies

FWP Number: 58926

Program Scope: This program develops new capabilities using the nation's synchrotron radiation facilities and applies them to key problems in materials science. In particular, we aim to play a leading scientific role at the Advanced Photon Source (APS). X-ray scattering studies take advantage of the high brilliance APS x-ray source for in-situ studies of synthesis and structure of ultrathin films of complex oxides, and interfaces in electrochemical and catalytic systems. High-resolution angle-resolved photoemission is used to understand the nature of superconductivity in the High-T_c materials. Other thrusts focus on exploring science enabled by future facilities such as an x-ray nanoprobe, a high-energy photoemission facility, and a coherent, femtosecond x-ray source.

Major Program Achievements (over duration of support):
Vapor-Phase Epitaxy: We have used *in situ* x-ray scattering to understand the atomic-scale growth mechanisms and surface structures occurring during MOCVD growth of GaN and $PbTiO_3$. Homoepitaxial growth mode transitions and surface reconstructions were mapped as a function of process conditions for the first time.
Quasiparticles in High-T_c Superconductors. The nature of the carriers in high-T_c superconductors has been elucidated using angle-resolved photoemission. We have identified a particular point on the Fermi surface where the superconducting energy gap vanishes below T_c, and determined the nature of the excitations that dominate the properties of the system.
Nanoscale Ferroelectricity: The minimum system size needed to support ferroelectricity has long been a subject of debate. We have recently demonstrated ferroelectricity in the most confined perovskite system yet, namely $PbTiO_3$ films as thin as three unit cells.
X-ray Studies of Catalysis Under Near Atmospheric Gas Pressure: Adsorption of CO is one of the most important issues in catalysis because of its poisoning of catalytic activity. Using innovative in situ x-ray techniques, we established the long-range-ordered nature of the CO overlayer on the Pt(111) surface under (near) atmospheric pressure of CO gas. A previously unobserved high-density structure was discovered, and a temperature-pressure phase diagram including the CO desorption boundary was determined.
Ultrafast X-ray Experiments*:* We have developed techniques for observing the interplay between electronic and structural dynamics on the femtosecond time scale using ultrafast x-ray pulses coupled with laser excitation. These studies using ultrafast x-ray pulses are providing part of the scientific basis for the next generation of accelerator-based x-ray sources.

Program Impact:
The Synchrotron Radiation Studies group publishes an average of 30 refereed articles every year, typically including 4 articles per year in Physical Review Letters, Science, or Nature. These articles are highly cited; based on citation rate, our average paper is in the top 1% of papers in materials science.

Interactions:
This project provides expertise in synchrotron techniques to collaborations with several Materials Science Div. groups (esp. FWP 59001, 58307, 58930 and 58601), other ANL Divisions (esp. X-ray Science), and with researchers at more than 30 universities, academic institutions, and industrial laboratories worldwide.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
J. C. Campuzano was appointed Scientific Director of Univ. of Wisconsin's Synchrotron Radiation Center in 2002. Each year about two dozen invited talks are given by group members.

Personnel Commitments for FY2006 to Nearest +/- 10%:
Staff: J. C. Campuzano (50%), P. H. Fuoss (100%), N. Markovic (50%), V. Stamenkovic (50%), H. You (50%), G.B. Stephenson (40%); Visiting Faculty: M. Bedzyk (10%); Postdocs: F. Jiang (50%), D. Hennessy (100%).

Authorized Budget (BA) for FY04, FY05, FY06:
FWP58926: **FY04: BA** $1,340K **FY05: BA** $1,800K **FY06: BA** $1,660K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP:
Dynamics of Granular Materials

FWP Number: 58806

Program Scope: This program focuses on theoretical and experimental analysis of the physics of granular materials. We consider the experiments, the theory, and large-scale molecular dynamics simulations of partially fluidized granular flows in application to granular avalanches, effects of the particle anisotropy on collective motion, and dynamic self-assembly of microparticles in weakly conducting liquids subject to electromagnetic field.

Major Program Achievements (over duration of support):
Transverse instability of granular avalanches: Avalanche experiments on an erodible substrate are analyzed using the partial fluidization model of dense granular flows. The model identifies a family of propagating soliton-like avalanches with shape and velocity controlled by the inclination angle and by the substrate depth. At high inclination angles the solitons display a transverse instability, followed by coarsening and fingering similar to recent experimental observations. The primary cause for the transverse instability is directly related to the dependence of soliton velocity on the granular mass trapped in the avalanche.
Self-assembly and pattern formation in magnetically driven granular systems at liquid surface*:* We developed and refined a new method based on ac magnetic field modulation to orchestrate the self-assembly of an ensemble of magnetic microparticles suspended on a liquid surface. With this method, we created a novel snake-like magnetic structure out of 40-90 micron sized magnetic particles. Our research provides new opportunities for the design of the next generation of transparent conducting electrodes based on a self-assembled network architecture which can be used for new types of solar cells.
Micromechanics of cytoskeleton: We considered the effects of finite flexibility on the interaction of two microtubules with a molecular motor. Based on the numerical solution to the nonlinear elasticity equation, we show that the flexibility enhances the tendency of microtubules to align, which in turn, favors the formation of large-scale structures in the multi-tubules system. Moreover, for much softer filaments like actin, we observed that the action of the motor may result in the formation of multiple loops due to buckling of the filaments.

Program Impact:
Our phenomenological approach to non-equilibrium behavior, in general, and granular materials in particular, established it as a legitimate theoretical tool for the worldwide scientific community.
The manipulation of magnetic micro-particles provides a new means to create networks of conducting wires through self-assembly which can be applied to fabricate transparent conducting electrodes for the next generation of solar photovoltaic cells.
Control of bio-objects by dynamic self-assembly constitutes a new approach which can be applied to the emerging bio-chip and biofilm technologies.
Understanding of the physical mechanisms of cytoskeleton dynamics will result in the design of new generation of biomolecular materials with unique mechanical properties.

Interactions:
UC San Diego; U. of Kansas; LANL; Northwestern U.; Hebrew U. of Jerusalem, Israel; CEA Saclay, Fr.; ESPCI, Paris, France; U. of Arizona, Cambridge University, UK.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
7 papers in high-profile journals, 1 Physical Review Letters, 1 Reviews of Modern Physics, and 4 Physical Review E, 1 Physical Review B, invited book chapter in 2005; 8 high-profile invited talks at international conferences, including a lecture course, 3 invited seminars and colloquia, 1 month invited professorship at ESPCI, Paris; one patent license on transparent conducting coating is pending.

Personnel Commitments for FY2006 to Nearest +/-10%: I. Aronson (70%), W. Kwok (30%), A. Snezhko (80%), Maxim Belkin (50%).

Authorized Budget (BA) for FY04, FY05, FY06:
FWP58806: **FY04:** BA $580K **FY05:** BA $500K **FY06:** BA $872K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and/or subtask Title under FWP:
Superconductivity and Magnetism

FWP Number: 58906 (includes 58823 through Sept. 2004)

Program Scope: This program makes in-depth experimental and theoretical investigations of fundamental phenomena in novel superconducting and hybrid materials at all length scales. Using nanotechnology tools for physics, we engineer novel structures whose small dimensions and electronic tunability facilitate the exploration of new phenomena and devices arising from confinement, proximity, and collective effects which could dramatically alter the physical properties and response to external fields and currents. We maintain leading programs in synthesis, experiment and theory, deriving strong benefit from their synergy.

Major Program Achievements (over duration of support):
Nanostructured and hybrid superconductors: We pioneered the fabrication of a novel crystal-heterostructure system which enables the study of vortex confinement and proximity effects at an unprecedented atomic scale with scanning tunneling microscopy (STM). The fabrication route combines the purity of single crystal $NbSe_2$ with focused-ion-beam nano-patterning and metal evaporation, resulting in atomically flat surfaces and clean metal/superconductor interfaces. Using a low temperature/high magnetic field STM, we imaged a collection of single vortices undergoing a structural transformation with increasing field due to confinement effects [Phys. Rev. Lett. 95, 167002 (2005)]. In addition, we fabricated and tested a novel magnet-superconductor hybrid system where a magnetic strip domain deposited on top of a superconductor could be used to control anisotropic vortex penetration in the underlying superconductor. We developed a novel procedure based on metal vapor transport to transform nanowires of $NbSe_3$ into superconducting NbN nanowires and nanoribbons. They provide a new stage for transport measurements to explore quantum and thermal phase slip phenomena. We pioneered new electrochemical deposition techniques for synthesizing type I superconducting Pb 3D mesocrystals with self-assembled geometries. These crystals exhibit confinement effects leading to a giant vortex state characterized by 'inherent' vortex pinning where the barrier to vortex entry/exit is the superconducting electron density.
New superconducting materials: We synthesized the newly discovered 11.6K graphite intercalated superconductor CaC_6 and mapped out its superconducting phase diagram with micro-calorimetry. We found a rather low anisotropy of $\Gamma \approx 3.7$, highlighting the importance of the metal-derived s-band in the formation of superconductivity. We determined a very large Ca-isotope effect coefficient $\alpha_{Ca} \sim 0.5$ demonstrating that CaC_6 is a phonon-mediated s-wave superconductor in which Ca-phonons play a dominant role.
Vortex physics: We developed a theory for the crossing Josephson/pancake vortex lattices in highly anisotropic BSCCO superconductor which quantitatively explained the existence of new vortex phases such as the chain states. The theory also promotes a new scheme using magnetic fields to control the viscosity of moving Josephson vortices. Our theoretical analysis of electromagnetic radiation emanating from Josephson-junction structures described the mechanism which converts Josephson oscillations into radiation and evaluated the radiation power and conversion efficiency and derived the criteria to ensure the stability of coherent steady states. Combining Josephson plasmon oscillations with photonic principles, we developed a new principal means to extract surface terahertz emission from meso-scale BSCCO mesas with metallic Bragg gratings (patent disclosure). We demonstrated an upper limit to the irreversibility line in YBCO crystals resulting from a vortex line tension transformation [Nature Physics 2, 402 (2006)].
Emerging areas: New work on nanophotonics demonstrated semi-circularly arranged nanoholes in thin metal films act as point sources of surface plasmons which can be focused into a high intensity, sub-wavelength spot. The electric field in this spot is strong enough to induce non-linear optical phenomena needed for photonic logic. We demonstrated enhanced Raman scattering from rhodamine 6G deposited in the focal spot. Our technique offers enhanced fidelity of the Raman Spectroscopy of nano-volume analytes over conventional SERS techniques. H_2 research-developed patentable ultra-fast response H_2 sensors based on nano-granular Pd films (2006 R&D 100 award).
Program Impact: Meso-crystal work in Science Editors' Choice highlight (2004); Surface plasmon work featured in Laser Focus World (2005), Science (311, 189 (2006)), Photonics Spectra and the Virtual Journ. of Nanoscale Science & Technology; H_2 nanosensors featured in Nanotechnology Now and Science Daily.

Interactions: Our collaborations extend within MSD, CHM, BIO, MTI, CMT, CNM, APS and worldwide.

Recognitions, Honors and Awards: Editorship Physica C (W. K. Kwok); NHMFL program/user committee (U. Welp); Patents related to Magneto-optic Current Sensor (#6,630,819), Near-field Magneto-optical Microscope (#6,972,562) and Superconducting MEMS (#6,638,895); Winner of the 2006 R&D 100 Award and Micro/Nano 25 Award on ultra-fast H2 sensors; V. Vlasko-Vlasov elected APS Fellow.

Personnel Commitments for FY2006 to Nearest +/- 10%: W. K. Kwok (30%), G. Karapetrov (75%), A. Koshelev (25%), M. Iavarone (50%), V. Vlasko-Vlasov (20%), M. Vinokur (20%), U. Welp (60%), D. Rosenmann (20%), Zhili Xiao (20%)

Authorized Budget (BA) for FY04, FY05, FY06:
FWP 58823 FY04: combined with 58906
FWP 58906 FY04: BA $1,010K **FY05:** BA $940K **FY06:** BA $889K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and/or subtask under FWP:
Emerging Materials

FWP Number: 58916 (including FWP 58802 through Sept. 2004)

Program Scope: The Emerging Materials effort explores the fundamental science of complex materials exhibiting collective electronic, magnetic and structural behavior. Materials synthesis is integrated with properties measurement to reflect our philosophy that these should be synergistic: new materials expose novel phenomena and call for innovative measurements, while a deep fundamental understanding demands new or higher quality materials. We emphasize low-dimensional systems via tailored crystal structures. Present and future research concentrates on metal-insulator transitions (MIT), phase competition and short-range order, new geometrically frustrated magnets and quantum critical materials. We include exploratory and strategic syntheses, where the latter is a targeted approach to extract the science in known materials. We grow crystals using zone, flux and vapor transport methods and by high-pressure synthesis. Property measurements discover and illuminate key issues focusing on electronic and magnetic interactions, and importantly provide immediate feedback to the materials grower that propels forward the synthesis program. Together these help elucidate the mechanisms underpinning, e.g., high-T_C superconductivity, the MIT and the delicate balance between short- and long-range order in transition metal oxides and chalcogenides.

Major Program Achievements (over duration of support):
We discovered that the outermost bilayer of bilayer manganites, alone, is an intrinsic insulating nanoskin with no ferromagnetic order while the next bilayer is a metal with magnetism. The result plus ARPES data from two collaborators (Shen and Dessau) establish our crystals as the 'gold' standard for manganite surface studies.
Our growth of $La_{1-x}Sr_xCoO_3$ crystals has enabled inelastic neutron scattering studies that suggest a model of dynamic orbital ordered clusters leading to competition between ferro- and antiferromagnetic coupling.
Synthesis of $YBaCo_4O_7$ material demonstrates that long-range antiferromagnetism is the true ground state in this nominally frustrated Kagomé system. We demonstrated that the geometric frustration inherent to the Kagomé units is broken by a structural phase transition, allowing long-range magnetic order to prevail.
High-pressure synthesis has delivered new materials for exploration of magnetic exchange. They are heretofore unknown double perovskites $CaCu_3Fe_2M_2O_{12}$ (M=Ta,Nb,Ru) and higher Cr substitution in $SrRu_{1-x}Cr_xO_3$. We have also isolated a high-pressure state of TaS_2 with T_c=3.5 K, four times higher than ambient pressure samples.
Novel vapor synthesis of nanowires of TaS_3 represents the first clear example of the charge-density wave (CDW) transition in a self-assembled nanowire. Our synthesis method is used to explore the effect of confinement on the CDW state of $NbSe_3$ and to generate superconductors of $NbSe_2$ and TaS_2.
Our timely synthesis of MgB_2 enabled our tunneling data to first identify self-energy effects due to interband quasiparticle scattering and also the absence of additional interband scattering after 10% C doping.
Our rapid response to intercalated graphite led us to conclude that CaC_6 is a strong-coupled superconductor, based on isotope-effect and tunneling measurements. This helps clear up some inconsistencies.
Purification of melt-grown crystals of bilayer manganites shed light on competing phases near two orbitally ordered states. The very narrow compositional range of stability challenges our understanding of highly correlated electron systems.

Program Impact: Our program boasts >319 publication citations (for papers published in the past three years). Our world-renown synthesis effort addresses the most exciting science and often drives the research agenda of internal and external collaborators. Our tunneling and anisotropic transport programs are at the cutting edge of research worldwide. In three years, our research has produced over 77 refereed papers with 17 in high visibility journals (PRL, Nature or Science), 25 in PRB, and >25 invited talks (3 at major international conferences).

Interactions: Internal: Intense Pulsed Neutron Source; Advanced Photon Source; and Electron Microscopy Center. External: Universities and laboratories worldwide. In the past three years, about 450 samples have been sent to over 37 unique collaborations, demonstrating the scope of outreach and impact our program delivers.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
John F. Mitchell: 2006 University of Chicago Distinguished Performance Award (with Osborn/Rosenkranz).
David G. Hinks has notably achieved 60 publications over his career with 60 or greater citations each.

Personnel Commitments for FY2006 to Nearest +/- 10%:
Staff: K.E. Gray (group leader) 80%, J.F. Mitchell 100%, H. Zheng 100%, D.G. Hinks (part-time staff) 40%.
Postdoc: T. Wu (50%), Y.S. Hor (100%), J. Hill (50%), P. Barnes (50%), R. Macaluso (25%). Visiting Scientist: A. Bhattacharya (50%), Qing'An Li (30%), L. Ozyuzer (30%). Graduate students: D. Mazur (100%), C. Kurter (100%)

Authorized Budget (BA) for FY04, FY05, FY06:

FWP58802	**FY04:** **BA** $725K	**FY05:** combined with FWP 58916		
FWP58916	**FY04:** **BA $**645K	**FY05:** **BA $** 1,397K	**FY06:** **BA $**1,245K	

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP:
Magnetic Films

FWP Number: 58918 (including FWP 58830 thru Sept 2005)

Program Scope: Our goals are to create, explore and understand novel nanomagnetic materials and phenomena. Our interests include the physical, chemical and metallurgical properties of artificially layered superlattices, sandwiches, wedges, ultrathin films, surfaces, and includes lithographic patterning and self-assembly. The task is to identify fundamentally new phenomena associated with the competition between spatial and magnetic length scales and proximity effects. We want to understand the ultimate limits of miniaturization, and to work to transform the art of nanomagnet fabrication into a science. We tailor properties via preparation conditions and manipulation of dimensionality for structures grown via sputtering, molecular beam epitaxy, and novel patterning and templating strategies. We explore exchange-coupled heterostructures and those formed with superconductors, insulators and antiferromagnets. We utilize surface magneto-optic Kerr effect (SMOKE), wideband microwave resonance, and synchrotron probes, and operate Brillouin and Raman scattering facilities. We study basic magnetization dynamics, magneto-transport, and magneto-optic phenomena. The new phenomena that we explore extend our basic understanding of nanostructured magnetic materials and lay the foundations for emergent technologies.

Major Program Achievements (over duration of support):
Exchange Biased Vortices*:* We investigated the magnetic behavior of exchange biased vortex structures and showed that as a function of applied field direction the exchange coupling can give rise to a transition from a magnetization reversal via vortex nucleation and annihilation to one of coherent rotation. We showed that this crossover could be tailored in accordance with prediction derived from a simple geometric model. In addition it is possible to imprint a vortex structure into the antiferromagnet, which stabilizes the vortex state and can give rise to novel asymmetric hysteresis loops. The results show that exchange biased vortices are an ideal model for studying the effect of interfacial coupling in magnetic nanostructures, since their magnetization reversal can be described analytically.
Magnetic Soft Mode Transitions: Submicron cobalt dots with competing in-plane magneto-crystalline and shape anisotropies were investigated and found to possess different domain patterns in remanence depending on field history. We relate this unusual behavior to a soft mode that triggers a phase transition. For example, stripe domains are generated by a standing wave mode that has the same spatial structure as the stripes when the external field is along the long axis of the bar. This mode goes soft at a second-order phase transition where the stripe domains emerge. For other field directions the phase transition can be first order.
Coherent Brillouin Scattering: We used Brillouin light scattering to demonstrate that inelastic light scattering from an array of Permalloy particles driven by a microwave magnetic field is a coherent phenomenon in which the scattered radiation is observed only at diffraction angles corresponding to the reciprocal lattice of the array. This technique is being used to study the hybridization of the uniform ferromagnetic mode with other modes of the particle array and to study the non-linear effects at high microwave power.
Exchange-Spring Interfaces: Sm-Co/Fe exchange-spring bilayers with graded interfaces exhibit enhanced exchange coupling effectiveness. We examined the element- and depth-resolved magnetization reversal process using x-ray resonant magnetic scattering (XRMS) magnetometry. Using model concentration profiles in combination with micromagnetic simulations, we simulated demagnetization curves that agree with the XRMS results and with electron microscopy observations. The XRMS results reveal that the enhanced exchange coupling effectiveness is due to the intermixing in the interfacial region and that the diffused Co behaves similarly to the surrounding Fe.

Program Impact: The laterally confined nanomagnet program, started in mid-FY01, was a winner of the DOE-BES competition entitled: Complex Systems: Science of the 21st Century. We (i) helped lead the theme on Electron and Magnetic Materials and Devices at Argonne's new Center for Nanoscale Materials, (ii) coordinated the DOE CSP project on Nanocomposite Magnets for ten years, and (iii) provide novel samples to a broad user community at the DOE synchrotron and neutron sources and electron microscopy centers.

Interactions: Our collaborations extend within MSD, CNM, BIO, MCS, CHM, IPNS, XFD-APS and worldwide.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
2003 UC-ANL Distinguished Performance Award (SJ); 2001 AVS Thornton Award (SB); 2007 APS Adler Award (SB); since 2001 a group total of over 100 invited talks and 35 invited participation as co-organizer or program/advisory committee of major meetings (*i.e.* APS, AVS, ICM, ICMFS, MMM, MRS, SRMS, DOE, NSF.)

Personnel Commitments for FY2006 to Nearest +/- 10%:
S. Bader(50%), M. Grimsditch(100%), J. Jiang(100%), A. Hoffmann(100%), V. Novosad(100%), F. Fradin (10%).

Authorized Budget (BA) for FY04, FY05, FY06:
FWP 58830 **FY04**: **BA** $445K **FY05:** combined with 58918
FWP 58918 **FY04:** **BA** $950K **FY05:** **BA** $1,620K **FY06**: **BA** $1,590K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020203

FWP and possible subtask under FWP:
Condensed Matter Theory

FWP Number: 59001

Program Scope: Condensed matter theory research programs in MSD are currently carried out in the areas of superconductivity, spectroscopy, magnetism, and nanoscience. More detail is available at http://www.msd.anl.gov/groups/cmt/

Major Program Achievements:
Superconductivity: Used a percolation model of superconducting and normal regions to describe the doping dependence of the superconducting transition temperature, and the linear temperature dependence of the resistivity in the normal state, of cuprates.

Spectroscopy: Developed a new method to calculate the dynamic spin response using photoemission spectra as input, and found results consistent with a spin exciton picture for the collective modes of cuprate superconductors. Discovered a linear temperature dependence of the Fermi arc length in the pseudogap phase of the cuprates that implies the existence of a d-wave node at zero temperature.

Magnetism: Analyzed the Kondo volume collapse model near its quantum critical point and found a novel bifurcation of the $\alpha-\gamma$ phase line in the pressure-temperature plane due to quantum fluctuations. Found a linear temperature dependence of the resistivity near the quantum critical point of the Kondo-Heisenberg model.

Nanoscience: Predicted ferromagnetism in quantum wires due to exchange interactions in the low density limit, and elucidated the importance of 3-particle and 4-particle ring exchange. Predicted the evolution of the electronic structure of quantum wires as their thickness increases. Studied the power law divergence of the tunneling density of states in quantum wires as well as the temperature dependence of this divergence.

Program Impact:
Work, particularly in the areas of superconductivity and mesoscopics, is recognized world-wide, with numerous invited talks given by Drs. Abrikosov, Matveev, and Norman. The collaboration on photoemission in cuprate superconductors in the past several years led to 39 papers in Nature, Physical Review Letters, and Physical Review B. Dr. Norman has 29 papers and Dr. Matveev has 13 papers with over 50 citations. Dr. Abrikosov is the author of many highly cited papers in physics, as well as two well-known books.

Interactions:
This program involves collaborations with ANL Materials Science programs on Superconductivity and Magnetism (58906), Synchrotron Radiation Studies (58926), Neutron and X-Ray Scattering (58701), and Emerging Materials (58916); and with programs at the University of Illinois at Chicago, Northwestern University, Ohio State University, University of Minnesota, University of South Carolina, University of Washington, University of Wisconsin-Madison, John Hopkins University, and Ames Laboratory. Also, collaborations exist with the University of Toronto (Canada), SPhT-Saclay (France), RIKEN, and Hokkaido University (Japan).

Recognitions, Honors and Awards:
Dr. Abrikosov is a member of the National Academy of Sciences and the Royal Society of London. He received the Nobel Prize in Physics in 2003, and has received many honorary degrees as well. Dr. Norman received the University of Chicago Distinguished Performance Award in 1999. Both are Fellows of the American Physical Society. Dr. Matveev is a Sloan Fellow.

Personnel Commitments for FY2006 to Nearest +/- 10%:
A. Abrikosov (100%), K. Matveev (100%), M. Norman (100%), P. Sharma (100%), I. Paul (100%), V. Vinokur (50%), A. Koshelev (50%)

Authorized Budget (BA) for FY04, FY05, FY06:
FWP59001 **FY04:** BA $1,173K **FY05:** **BA $**1,100K **FY06:** **BA $**1,350K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020203

FWP and subtask Title under FWP:
Materials Theory Institute

FWP Number: 59002

Program Scope: This program carries out forefront investigations via assembling national and international visitor research teams with complementary expertise tailored to important emerging problems in the field of materials sciences. The extensive visitor programs attract and bring together world-leading scientists for collaborative joint projects in direct support of DOE's mission. The visits can last from a few days to several months.

The program currently focuses on the physics of nanostructured materials and hybrid systems and soft condensed matter. The research projects are developed in close collaboration with MSD's experimental programs. Current research is focused along the following major themes: (1) Transport properties of arrays of quantum dots; (2) Quantum phase transitions in low-dimensional and disordered structures; (3) Quantum charge and spin transport in hybrid and disordered materials; and (4) noise and decoherence effects in nanodevices.

Major Program Achievements (over duration of support):
Many electron theory of 1/f noise in hopping conductivity**:** One of the central problems of the contemporary condensed matter physics is a problem of the universal character of the so-called 1/f-noise, which is the characteristic feature of a glassy system and glassy behavior. One of the exemplary systems that exhibit glassy properties is a hopping semiconductor, and the origin of the 1/f noise in semiconductors had been a subject of the intense debate for decades. We have put forward a novel model resolving the long-standing puzzle of decreasing noise intensity with the temperature growth in the important low-temperature regime and developed criteria for finding the lower frequency bound for the 1/f noise. We have shown that 1/f noise in the variable-range hopping regime is related to transitions of many-electrons clusters (fluctuators) between two almost-degenerate states. Giant fluctuation times necessary for 1/f noise are provided by the slow rate of simultaneous tunneling of many localized electrons and by large activation barriers for their consecutive rearrangements. The noise amplitude grows with the decreasing temperature because it is easier to find a slow fluctuator at lower temperatures [Phys. Rev. B **74**, 075205 (2006)]. Other theoretical achievements: theory of charge pumping through quantum superconductor-insulator-normal metal-insulator-superconductor contacts; theory of charge transfer between hopping insulator and superconductor: generalization of the Andreev processes – the novel time reversal reflection mechanism was introduced; theory of slow crack propagation in heterogeneous materials.

Program Impact:
Maintains global collaborative network: MTI – BNL – LANL – UofC – Northwestern University – University of Wisconsin – UCSD – Ruhr University – Köln University – TU Delft – Chalmers University – Oslo University – A F Ioffe Institute – CRTBT-CRNRS (Grenoble) carrying out joint projects on nanophysics and soft condensed matter physics, exchanging visits and conducting a chain of International Workshops on Nanophysics in US and Europe. Created the program on properties of nanostructured materials which is recognized as one of the world-leading program as evidenced by the numerous applications for participation in the Argonne Fall Workshops on Nanophysics. Advisory Committee recruited new active members to propose and design novel research topics and joint projects on the most demanding subjects, involving a wide community of researchers into DOE projects and exposing ANL achievements to the scientific community. New collaborations with University of Minnesota, Columbia University, and Tulane University (New Orleans) were established. During the period of October 1, 2005 – September 30, 2006 the program activity resulted in 19 publications (including 7 PRLs and 9 PRBs) and 25 invited talks at the international conferences.

Interactions:
Internal: Condensed Matter Theory, Emerging Materials, Magnetic Films, Synchrotron Radiation Studies (MSD)
External (In addition to listed above): Princeton University; Syracuse University; University of Florida; Harvard; Leiden University; Helsinki Technological University; Weizmann Research Institute, Israel; Tel Aviv University, Israel; Hebrew University, Jerusalem, Israel; Coherentia-INFM, Rome, Italy; Landau Institute, Moscow; Institute for Microelectronics, Nizhny Novgorod, Russia.

Recognitions, Honors and Awards (at least in some part attributable to support this FWP or subtask):
Editorship Central European Journal of Physics [2003-present – V. Vinokur]

Personnel Commitments for FY2006 to Nearest +/- 10%:
V. Vinokur (80%), A. E. Koshelev (20%), I. Beloborodov (80%), A. Lopatin (50%), A. Glatz (100%)

Authorized Budget (BA) for FY04, FY05, FY06:
FWP59002 **FY04 BA** $267K **FY05: BA** $250K **FY06: BA** $250K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020203

FWP and possible subtask under FWP:
Quantum Computation with Electron Spins

FWP Number: 59003

Program Scope: One of the most exciting phenomena at the nano-scale is that of quantum phase coherence and its application to quantum computing because of the powerful potential in areas of large database searches, large number factorization, and quantum mechanical simulation of physical systems The grand challenge is to develop scalable arrays of quantum bits (qubits) and the logic gates of a quantum computer. In this research program we develop electron spin resonance (ESR) techniques to manipulate and both scanning tunneling microscopy-ESR (STM-ESR) and radio frequency-single electron spin transistor techniques to measure single electron spins in arrays of nanoscale quantum dots in order to form the scientific underpinnings of an electron spin quantum computer. The basic qubit consists of endohedral nitrogen in C_{60}, which has a long spin phase coherence time. We also make use of biological processes to attach C_{60} to DNA networks to form the array of interacting qubits, and advanced lithographic processes to form address gates and the readout tunnel junctions necessary for a quantum computer.

Major Program Achievements:
A key task is to prepare the qubits of endohedral nitrogen in C_{60}. A new C_{60} effusion cell has been combined with the Kaufman ion source and a shutter to increase the production rate of endohedral N in C_{60}. Using ESR measurements of the narrow 3 line hyperfine split spectra of N^{14} in $N@C_{60}$ a hundred-fold increase in its concentration has been determined. A new automated preparatory HPLC chromatography system has been put into operation, which allows for much greater throughput for separating $N@C_{60}$ from C_{60}. After HPLC separation we find a dramatic elimination of the impurity ESR signal relative to the $N@C_{60}$ signal. However, because of the overlap of ESR inactive C_{60} with $N@C_{60}$ in the UV detector on the HPLC, we are planning to obtain a mass spectroscopy detector that will enhance our separations capability.

We have developed the chemical protocols required to attach C_{60} to PNA using carboxyl groups. We have succeeded in making the PNA attachments, but have not yet demonstrated the attachment of the PNA complex to DNA, which will serve as our template for a one dimensional array of $N@C_{60}$ qubits with very well defined separations. Note we plan to use N^{14} and N^{15} for the distinguishable qubits.

We have designed and constructed a new STM with both pico-ampere sensitivity for single molecule tunneling spectroscopy and a highly sensitive radio frequency receiver for ESR detection of single electron spins. The ESR-STM system is currently undergoing tests. A novel high speed signal digitizer is being implemented in-order to enhance signal to noise of the ESR signals.

Program Impact:
A number of presentations on the early stages of the research in this program, which was initiated in July 2005, were made at conferences, including the November MRS meeting, the March APS meeting, and at an EPR Symposium in July 2006.

Interactions:
Our collaborations extend within 4 groups in MSD and within CNM, CHM, BIO and Northwestern University.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Dr. Fradin is a fellow of the American Physical Society.

Personnel Commitments for FY2006 to Nearest +/- 10%:
F. Fradin (60%), J. Schlueter (0%), O. Auciello (0%), C. Liu-postdoctoral appointee (0%), P. Messina-postdoctoral appointee (100%), L. Zhang-postdoctoral appointee (0%), T. Rajh (0%).

Authorized Budget (BA) for FY04, FY05, FY06:
FWP59003 **FY04: BA** $0K **FY05:** BA $400K **FY06**: BA $377K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and/or subtask Title under FWP:
Nanostructured Thin Films

FWP Number: 57504

Program Scope: The Nanostructured Thin Films Program is an integrated effort involving synthesis, characterization, and computer simulation. Research within the program is on fundamental science related to the synthesis of nanostructured carbon materials, especially the development of novel plasma and growth chemistries and also quantum chemical computational studies of growth processes and electronic structure. Work is focused on the transport properties including thermal and electrical conductivity of nanocrystalline diamond and composites involving diamond either at ANL or via collaborations with leading researchers at other national labs, and universities. The program also exhibits a high degree of world leadership in advancing the characterization of these materials using a variety of techniques including state-of-the-art electron microscopies and synchrotron-based techniques, and in so doing leverages many of the unique resource available only at ANL. The program also supports a computational methods development effort that is used in these programs as well as others, and is recognized worldwide.

Major Program Achievements (over duration of support):
Intensive studies of n-type ultrananocrystalline diamond films discovered at Argonne have led to new understanding of the remarkable electron transport, electrochemical, electron field emission, high temperature diode and optical properties of the films. Detailed work has uncovered an insulator-metal transition as nitrogen is added to the synthesis gas resulting in conductivities of several hundred S/cm. The transition to the metallic state has now been found to be due to formation of a new morphology that can be characterized as diamond nanowires. Raman spectroscopy has revealed that the sheath is likely composed of a nanocarbon material resembling a copolymer of polyacetylene and polynitrile. Optical emission studies have given insight into the growth mechanism. Theory is being used to provide fundamental new insight into the UNCD films and carbon composites including the electrical conductivity mechanism in the films, the kinetics of the growth mechanism, the location of nitrogen in nanodiamond particles, and pathways to formation of composites between UNCD and carbon nanotubes. For example, the competing growth and nucleation processes involved in the formation of UNCD films have been investigated using extensive quantum chemical simulations and have been used to explain the dependence of the morphology of the films on temperature. Also, a recent theoretical study has revealed a new type of defect in carbon nanotubes that can be used to modify their reactivity for making new composites and their electronic properties for thermoelectrics. The quantum chemical methods development work has resulted in methods having a new level of accuracy that will have many applications in materials chemistry and other fields.

Program Impact:
This program is widely recognized as a leading program in the world on nanostructured diamond materials. The work has lead to numerous invited talks and publications including articles in Nature-Materials, Advanced Materials, Langmuir, Physical Review Letters, and several in Applied Physics Letters. The program organized and hosted a major international diamond conference (The 8th Applied Diamond Conference/NanoCarbon 2005) at ANL in May 2005.

Interactions:
This program has extensive collaborative relationships within the Materials Science Division, Argonne National Laboratory, and throughout the world. We also make substantial use of major user facilities at ANL such as the Intense Pulsed Neutron Source, the Electron Microscopy Center, the Laboratory Computing Center, and Center for Nanoscale Materials.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
2000 MRS Medal (Dieter Gruen); 2003 R&D 100 Award, ISI Highly Cited Researcher in Chemistry, 1980-1999 (Larry Curtiss)

Personnel Commitments for FY2006 to Nearest +/- 10%:
L. A. Curtiss (70%), D. M. Gruen (100%), P. Zapol (10%)

Authorized Budget (BA) for FY04, FY05, FY06:
FWP57504 **FY04 BA** $1034K **FY05 BA** $924K **FY06 BA** $825K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Nanostructured Biocomposite Materials for Energy Transduction

FWP Number: 57525

Program Scope: This program involves the synthesis and characterization of nano- or meso-structured materials that either mimic or exploit biomolecules to store and transduce energy. The program involves three integrated tasks focused on developing biomolecular materials for energy transduction. Specifically, these include the synthesis of biomimetic soft materials (complex fluids, ionogels) for organizing a variety of biomolecules (e.g., soluble and membrane proteins) or nanoparticles (semiconductors or metals), synthesis of hard materials (rigid mesoporous inorganic frameworks, ferroelectric thin films, carbon nanostructures) tailored for enhanced electronic transport or photon-induced processes and the integration of these soft and hard materials to from robust, functional biocomposites.

Major Program Achievements (over duration of support):
Developed three families of thermoresponsive soft nanostructures whose supramolecular architecture and physical properties can be altered by modest changes in temperature. Demonstrated the utility of these materials in controlling the collective properties of encapsulated guests (host-mediated energy transduction). Materials proven as biomimetic and biocompatible soft tunable frameworks for the stable encapsulation of water soluble and membrane proteins.

Developed ionic-liquid–based gels whose nanostructure can be tuned by controlled addition of water. Demonstrated that these ionogels can serve as templates, directing the particle morphologies of nanoparticles photochemically synthesized within them to yield previously unattainable particle shapes and thus, novel optical properties. Synthesized polymerizable ionic liquids that form liquid-crystalline, polymeric hydrogels and organogels. Used ionic liquid polymers to fabricate an organogel with optical properties (plasmons) tunable from the visible to NIR.

Successfully applied combinatorial phage display methods to identify a circularly constrained heptapeptide sequence that strongly associates with perovskite ferroelectrics that can now be used to selectively pattern ferroelectric thin films and couple and actuate tethered biomolecules.

Asymmetrically hardwired a genetically engineered photosynthetic protein to an external circuit and evaluated its electronic transport properties proving that is can function as a (diode) molecular circuit element.

Program Impact:
Hybrid soft-hard materials that can stabilize active biomolecules have been synthesized, thereby laying the groundwork for the assembly of functional, protein-based materials.

Interactions:
Internal: Condensed Matter Physics and Materials Engineering Physics sections of MSD, CNM, APS, and Bioscience. External: Northwestern University, University of Puerto Rico, University of Chicago, University of Wisconsin- Madison

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Named 1 of "20 people you don't know who are changing the world" by iBIO (the Illinois Biotechnology Industry Organization) - M. Firestone
James Flack Norris Award for Physical-Organic Chemistry, Professor Michael R. Wasielewski

Personnel Commitments for FY2006 to Nearest +/- 10%:
M. A. Firestone (60%), P. Zapol (20%), L. E. Iton (100%, STA), P. Laible (30%), S. Adiga (50%, Post-doc), Burns (100%, Post-doc), Reedy (100 %, Post-doc), M. R. Wasielewski (subcontract to Northwestern University).

Authorized Budget (BA) for FY04, FY05, FY06:
FWP57525 **FY04:** **BA** $731K **FY05:** **BA** $675K **FY06:** **BA** $650K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Molecular Materials

FWP Number: 58510

Program Scope: World-class fundamental research on materials with the aim to develop new chemistry for synthesizing molecular and nanoscale building blocks to create macroscopic materials that have unique architectures, and ultimately to create new materials that have novel functional properties. The program successfully integrates expertise in synthesis, physical characterization, and computer simulations to address some of the most challenging problems in materials chemistry. The research encompasses two related thrusts. The first is the tailoring of molecular framework architectures through supramolecular chemistry. The second involves the control of size, shape, and functionality of nanoscale building blocks such as nanoparticles, nanowires, and nanotubes and the integration of these units into materials with desired properties. In addition, a computational component provides theoretical insight into various aspects.

Major Program Achievements (over duration of support):
(1) The first coordination polymer with bifluoride ions as building units has been synthesized. The bifluoride (HF_2^-) ion contains the strongest hydrogen bond known and there are no previous examples of bifluoride bridged metal centers. This work has demonstrated for the first time that this innovative molecular building block can be rationally incorporated into molecular frameworks and that magnetic superexchange can be mediated through hydrogen bonding. (2) A new ultramicroporous metal organic framework material has been synthesized with triazole linkers that has potential for separation of impurities from H_2. Molecular dynamics simulations indicate that H_2 will diffuse rapidly through the pore structure while slightly larger molecules will not. (3) A new type of framework material for catalysis that uses an electrochemical procedure to make a porous alumina and surface modification by atomic layer deposition has been developed. (4) Ordered arrays of nanowells on aluminum oxide surfaces have been made using electrochemical techniques. These nanowells are being explored for novel ways to make sensors. (5)AAO has been used as a template to make nanowires, nanotubes, antidot arrays with novel properties such as a new type of Pd nanotube that has higher sensitivity and response time to hydrogen than conventional Pd thin film sensors. (6) Studies of gold nanocrystals have revealed controlling factors of synthesis and assembly. Experiments on Co and FePt nanocrystals have demonstrated that both the ligand type and the concentration of ligand affect the formation of particles, resulting in different sizes and shapes. (7) Computational studies have revealed new insight into the shapes of gold nanoparticles and their phase transitions.

Program Impact:
The synthesis effort is leading to new and exciting nanostructured materials with potential for applications in sensors, catalysis, photonics and advanced electronic and magnetic materials. Our unique capabilities in the design, synthesis, and characterization of new materials have led to close interaction with other groups in the Materials Science Division, as well as the worldwide scientific community. We have also been closely involved with the development of new lab-wide initiatives on hydrogen, catalysis, solar energy, solid state lighting, and biomaterials as well as the Center for Nanoscale Materials.

Interactions:
Internal— Collaborations with Superconductivity and Magnetism, Magnetic Films, Synchrotron Radiation and Surface Chemistry Groups. Participation in new initiatives on Biomaterials, Hydrogen, Catalysis, and Solar. Collaborations with other Argonne divisions including the Center for Nanoscale Materials, Chemistry, Advanced Photon Source, Intense Pulse Neutron Source, Energy Technology, and Math and Computer Sciences.
External— Over 50 collaborations with national and international research facilities, such as the University of Chicago, Northwestern University, University of Illinois-Chicago, Indiana University, etc.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Over 100 publications in the past three years, numerous invited review articles, one review book, over 30 invited talks. Organized symposia and workshops. Several of our papers have been selected for feature articles and journal covers have featured our research. Organic superconductor research was named one of the 100 top scientific discoveries funded by the DOE Office of Science. Numerous citations to papers, including one group member named a Highly Cited Researcher in Chemistry by ISI for the period 1981-1999 (Curtiss).

Personnel Commitments for FY2006 to Nearest +/- 10%:
H. Wang (80%), J. Schlueter (80%), U. Geiser (50%), L. Curtiss (10%)

Authorized Budget (BA) for FY04, FY05, FY06:
FWP 57502 **FY04:** combined with FWP 58510
FWP 58510 **FY04:** **BA** $1,024K **FY05:** **BA** $1,150K **FY06:** $900K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and/or subtask Title under FWP:
Directed Energy Interaction with Surfaces

FWP Number: 58600

Program Scope: The interaction of directed energy sources such as energetic ions, electrons, and photons with surfaces provides the basis for modifying, patterning and analyzing surfaces and nanoscale materials. This program investigates the fundamentals of these complex interactions over a wide range of conditions using several unique, world-class methods developed in our laboratory. These uniquely sensitive tools for trace analysis are also providing, for the first time, mass based analysis of materials with nanometer scale lengths.

Major Program Achievements (over duration of support):
We have built and demonstrated the world's most sensitive trace analysis mass spectrometer. The high useful yield (>30%) of this device opens the possibility for mass based analysis of nano-materials and the unique discrimination allows measurements in the ppt range. In this period high lateral (50 nm) and depth (1 monolayer) resolution has been added to make this instrument an imaging nanoprobe. This imaging capability has been supplemented with a microfocus electron source allowing secondary electron microscopy to be done *in situ*.

While mass spectrometry is a powerful method for analyzing surface bound species and for molecular imaging of tissue, it frequently suffers from difficulties in forming ions that are structurally and quantitatively representative of complex organic surface species, especially for multicomponent surfaces. A versatile strategy has been demonstrated at ANL to address these shortcomings: threshold single photon ionization (SPI) of desorbed neutral molecules that proceeds by localized ionization of a chemical tag bound to a molecular analyte. Work during this period has used previously discovered tags to investigate the quorum sensing behavior of biofilms. This work shows that the method is significantly more sensitive than conventional techniques. The study demonstrates detection of quorum sensing proteins in biofilms samples orders of magnitude smaller than conventional techniques.

Program Impact:
Directed Energy sources represent an important method for analyzing, patterning and modifying nano-materials. The instruments and fundamental studies here quantify the limits of these techniques for nano-material modification, functionalization and analysis. The trace analysis capability developed under this FWP leads the world for trace analysis at nanoscale dimensions.

Interactions:
Collaborative publications with a wide range of University (including University of Chicago, Washington University St. Louis, California Institute of Technology, University of Newcastle) and National Labs (ANL, SNL, and LLNL) have appeared in the last few years. Further, our unique tools are applied in collaborative research on problems of particular importance to DOE. This work includes studies of OLED solid state lighting studies funded by EERE.

Recognitions, Honors and Awards (at least in some part attributable to support under this FWP or subtask):
2001 Energy 100 Award (One of the best 100 scientific accomplishments of the 20th Century; DOE-BES)

Personnel Commitments for FY2006 to Nearest +/- 10%:
M. J. Pellin (25%), W. F. Calaway (70%), M. R. Savina (15%), Igor Veryovkin (15%)

Authorized Budget (BA) for FY04, FY05, FY06:
FWP58600 **FY04: BA** $530K **FY05: BA** $520K **FY06: BA** $520K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Fundamental Studies of Electrocatalysis for Low Temperature Fuel Cell Cathodes

FWP Number: 58601

Program Scope: This program focuses on fundamental, molecular-level study of the surfaces of electrocatalysts for the fuel cell cathode and the reactions occurring on them. We use the advanced x-ray techniques available at the Advanced Photon Source, complemented by electrochemical techniques, scanning probe microscopy, and theoretical modeling to investigate the mono- or sub-monolayer sensitive molecular orientation and short- and long-range structures of oxygen and oxygen-containing molecules, reaction intermediates, poisons, spectators, and the chemical states of surface atoms of electrocatalyst itself, in addition to the kinetic parameters of the reaction. The electrocatalysts include model catalysts and realistic catalysts of platinum and platinum alloys. We investigate in-situ electrocatalytic systems with varying degrees of complexity, ranging from single crystals, to designed nano-arrays, to real fuel cell catalysts, and to single nanoparticles. The basic knowledge obtained from this study can be used to guide the development of future electrocatalysts.

Major Program Achievements (over duration of support):
This is a new program awarded in June 2005. We created one-dimensional (111)-(100) nanofaceted platinum surfaces by annealing high-index surfaces of platinum crystals. The nanofaceted surface is a model system representing (111)-(100) faceted Pt Cubooctahedra nanoparticle. Unusually high oxygen reduction activities of the model system led us to propose a new cooperative crossover mechanism in oxygen-reduction catalytic activities. In this mechanism, the reaction intermediates were allowed to move to neighboring facets that are more active but starving due to limited supply of oxygen. We also fabricated two-dimensional array platinum nanoparticles supported on $SrTiO_3$ substrates using electron-beam lithography. At this point, we are focusing on understanding the fabrication processes, substrate-dependent epitaxial properties and nanoparticle shapes. In theoretical fronts, thermodynamic modeling based on density functional calculations was used to describe equilibrium shapes of supported Pt nanoparticles in various chemical environments. Also, a self consistent tight binding model for nonrelativistic platinum is ready to use for study of Pt surfaces and development of a method for including relativistic effects is being implemented and debugged. We also developed new x-ray techniques investigating chemical states of buried interfaces essential to the study of electrocatalysis model systems.

Program Impact:
The new x-ray technique enables us to investigate low-Z elements at interfaces that are typically invisible to hard x-rays capable of penetrating through electrolyte or other media burying the interfaces. The concept of cooperative crossover reaction mechanism has a potential for wide applications in understanding variety of catalytic activities. It will also guide design of new real catalysts and model catalysts. Heterogeneous, alloyed catalysts will be fabricated and tested.

Interactions:
Internal --- Advanced Photon Source, Center for Nanoscale Materials, Chemical Engineering Division.
External --- U. of Illinois at Urbana, Lawrence Berkeley Laboratory, U. of Minnesota, Kent State U.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
HY: Invited talk at Symposium on Surface Imaging /Spectroscopy at the Solid /Liquid, Krakow, Poland, May 28 – June 1, 2006.
NM: Invited Talk at Symposium on Surface Imaging /Spectroscopy at the Solid /Liquid, Krakow, Poland, May 28 – June 1, 2006.
WH: Workshop on Hybrid Atomisic Methods for Materials and Biological Systems, CECAM in Lyons, France, July 10-13, 2006

Personnel Commitments for FY2006 to Nearest +/- 10%:
H. You (30%), N.M. Markovic (10%), D. Myers (10%), G. Karapetrov (10%), P. Zapol (10%), 4.6 Postdocs

Authorized Budget (BA) for FY04, FY05, FY06:
FWP58601 **FY04** BA $ 0 **FY05** BA $ 760K **FY06** BA $960K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Biohydrodynamics

FWP Number: 58806-CD

Program Scope: This new program initiated in FY06 focuses on theoretical and experimental analysis of the physics of active biological objects such as bacteria, motor proteins interacting with bio-filaments and cytoskeleton dynamics. We consider the experiments, the theory, and large-scale molecular dynamics simulations of swimming bacteria on thin film geometry, interaction of microtubules and molecular motors, and constitutive relation for cytoskeleton dynamics.

Major Program Achievements (over duration of support):
Self-organization and control of active bioparticles**:** We initiated a new research direction which applies the theoretical and experimental aspects of dynamic self-assembly found in granular matter to the self-organization of active bio-organisms such as Bacillus subtilis and E. coli. The self-organization takes the form of coherent structures with sizes that are many times larger than those of the individual bacteria. We investigated the emergent collective behavior in dense bacterial colonies confined in a thin liquid film of controlled thickness and developed a new method of controlling the density of the bacteria colony by transmitting electric current, enabling studies of the scale of the emergent dynamic structures as a function of cell concentration. We developed a continuum mathematical model of this phenomenon to demonstrate that the primary mechanism of self-organization is associated with the shear flow induced deflection of bacteria orientation. In the near future we plan to develop a new generation of experiments aimed at the independent resolution of the hydrodynamic velocity field and flagellum orientation through high-speed fluorescent microscopy. The theoretical model will be validated by molecular dynamics simulations of elementary "swimmer" particles in a thin fluid film geometry.

Program Impact:
Control of bio-objects by dynamic self-assembly constitutes a new approach that can be applied to the emerging bio-chip and bio-film technology and targeted drag delivery.

Interactions:
UC San Diego; Northwestern U.; Hebrew U. of Jerusalem, Israel; CEA Saclay, Fr.; ESPCI, Paris, France; U. of Arizona, Cambridge University, UK, University of Wisconsin, Madison

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask): two papers submitted to Physical Review Letters; 8 high-profile invited talks at international conferences, including a lecture course, 3 invited seminars and colloquia, 1 month invited professorship at ESPCI, Paris; patent license on dynamic bacteria concentration is pending.

Personnel Commitments for FY2006 to Nearest +/-10%: I. Aronson (30%), W. Kwok (20%), A. Snezhko (20%), Maxim Belkin (50%), D. Rosenmann (30%).

Authorized Budget (BA): **FY04:** BA $-0-K **FY05:** BA $-0-K **FY06:** BA $524K